



Photolytic and photocatalytic degradation of fluoroquinolones in untreated river water under natural sunlight

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ABSTRACT

The photodegradation of some among the most frequently prescribed fluoroquinolone antibacterials (FQs) was investigated in untreated river water under solar light as well as under the same conditions in the presence of suspended TiO_2 . The drugs considered included ciprofloxacin (CIP), danofloxacin (DAN), enrofloxacin (ENR), levofloxacin (LEV), marbofloxacin (MAR) and moxifloxacin (MOX), the last two belonging to the most recent FQ generation. The experiments were carried out in lab-scale batch reactor at concentrations ($20\text{--}50\ \mu\text{g L}^{-1}$) comparable to those actually measured in surface waters, and the course of the reaction was monitored by high pressure liquid chromatography (HPLC) with fluorescence detector (FD). A first order kinetics was obeyed upon both direct photolysis and TiO_2 heterogeneous photocatalysis. The photoproducted intermediates were identified by HPLC with electrospray ionization tandem mass spectrometry (ESI-MS/MS) and the degradation paths were identified. It was concluded that direct irradiation caused fluorine substitution and reductive elimination, while photocatalysis caused oxidative degradation of the amine side-chain (most efficient with tertiary amines and five-membered cyclic amines). The latter one was a minor process upon direct photolysis and involved hydrogen abstraction by excited states or photoproducted radicals. Photocatalytic decomposition occurred at a rate from two to five times faster than direct photolysis for all of the drugs, except for CIP, that is roughly proportional to the amine oxidation potential. The kinetic constants ranged from 0.061 to $0.66\ \text{min}^{-1}$ in direct photolysis, from 0.22 to $2.78\ \text{min}^{-1}$ in the presence of TiO_2 . In the latter process, a 90% abatement of the concentration of these otherwise highly persistent drugs was obtained in ca. 15 min. This supports the contention that TiO_2 photocatalysis under solar light is a convenient and efficient method for the remediation of pollutants at the $\mu\text{g L}^{-1}$ levels despite the presence of other non-target matrix constituents. Noteworthy, TiO_2 side-chain photo-oxidation was equally effective in the further degradation of the primary intermediates at a rate comparable to that of the parent compounds. The degradation proceeded further so that it could be expected that the antimicrobial activity, related to the FQ quinolone core more than to the substituent pattern, could be effectively eliminated.

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1. Introduction

The persistence of drugs in the environment and their fate are the matter of increasing concern in recent years [1,2]. As an example, the widespread diffusion of fluoroquinolone antibiotics (FQs) in different ecosystems has been well documented [3–5]. These

antibacterial agents are largely prescribed both in human and veterinary medicine and are only partially metabolized in the body. Thus, a significant fraction is excreted as such, or to a lesser degree, as metabolites conserving the quinolone structure deriving from the addition of reactive functional groups or via covalent conjugation to polar molecules [6,7].

Furthermore, heterocycles such as FQs are only partially removed by wastewater treatment plants [7]. Such broad-spectrum antibiotics are thus present in the environment and can have a selective effect on microbial communities, thus stimulating bacterial resistance, even at very low concentrations [8,9]. Furthermore, the co-occurrence of multiple FQs must be taken into account in order to properly evaluate the total biologically effective levels [10].

Advanced oxidation processes (AOPs), such as ozonation [11,12], sonolysis [13], photolysis [1,14–16] and titanium dioxide

Abbreviations: AOP, advanced oxidation process; ACN, acetonitrile; CIP, ciprofloxacin; DAN, danofloxacin; DOM, dissolved organic matter; ENR, enrofloxacin; ESI-MS/MS, electrospray ionization tandem mass spectrometry; FD, fluorescence detector; FQs, fluoroquinolones; HPLC, high pressure liquid chromatography; LEV, levofloxacin; MAR, marbofloxacin; MOX, moxifloxacin.

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(TiO₂) photocatalytic degradation [10,17–21] have been recently applied for the remediation of FQs. Using TiO₂, an inexpensive and safe semiconductor as photo-oxidant, is an appealing possibility in the perspective of green chemistry, because it is active under natural sunlight [19]. TiO₂ has been extensively employed for the remediation of pollutants, such as herbicides [22,23], polycyclic aromatic hydrocarbons [24,25], chlorophenols [26–28] and many others [29–38].

Photoexcitation of TiO₂ causes the promotion of electrons from a filled valence band to an empty conduction band, giving rise to electron–hole pairs. The valence band holes migrate to the particle surface and react with adsorbed water to produce hydroxyl radicals •OH or ‘trapped holes’ (≡Ti^{IV}O•) generated by the combination of the holes photogenerated in TiO₂ valence band with water and dissolved molecular oxygen, whereas the conduction band electron reacts with adsorbed electron acceptors [17]. It has been demonstrated that direct UV–visible (UV-A/B) irradiation causes the decomposition of FQs in water and the main paths are defluorination and amine side-chain oxidation [1,14–16]. As for TiO₂ photocatalysis, this has been explored only for a few FQs, with scarce attention to the products structure. The available studies have been carried out in ultrapure (double-distilled or deionized) water at the ppm levels [17,19–21,39] and have assessed the effect of pH [21] and of the nature of free radicals [20] on the reaction kinetics.

The overall picture is further complicated by the fact that TiO₂ and FQs absorb light in the same wavelength region (300–370 nm) and thus the two processes may occur competitively and also the matrix constituents under environmental conditions, such as dissolved organic matter (DOM) or other xenobiotics [17], may have a role.

In view of the above, we embarked in exploring both direct photolysis and TiO₂ photocatalytic decomposition of six FQs, chosen among those most largely used for both human and veterinary purposes, *under actual environmental conditions*. Thus, the study was carried out at concentrations actually determined in surface waters, viz. at the µg L⁻¹ level [40–43], by sunlight irradiation of raw river water samples. The drugs were ciprofloxacin (CIP), danofloxacin (DAN), enrofloxacin (ENR), levofloxacin (LEV), marbofloxacin (MAR) and moxifloxacin (MOX), the last one belonging to the rapidly expanding “new generation” of FQs [21]. Quantitative analyses were performed by high pressure liquid chromatography (HPLC) with fluorescence detector (FD).

Structure attribution to byproducts was based on HPLC measurements with electrospray ionization tandem mass spectrometry (ESI-MS/MS). For these experiments more concentrated solutions (at mg L⁻¹ levels) were purposely irradiated. Results from photolysis and from photocatalysis have been compared in terms of conversion yields and byproducts structures.

2. Experimental

2.1. Chemicals and materials

All the chemicals employed were reagent grade or higher in quality and were used without any further purification. FQs standards and reagent grade HCOOH (>95%, w/w) were supplied by Fluka (Sigma–Aldrich, Milan, Italy), HPLC gradient grade acetonitrile (ACN) by VWR (Milan, Italy), H₃PO₄ (85%, w/w), HCl (37%, w/w) and NaOH anhydrous pellets (97%, w/w) by Carlo Erba (Milan, Italy). Ultrapure water (resistivity 18.2 MΩ cm⁻¹ at 25 °C) was produced in laboratory by means of a Millipore (Milan, Italy) Milli-Q system. FQs stock solutions of 300 mg L⁻¹ were prepared in methanol (0.1%, v/v 1 M NaOH) and stored in the dark at 4 °C for a maximum of three months. Working solutions of 6 mg L⁻¹ in 25 mM H₃PO₄

were renewed weekly. Degussa P25 titanium dioxide (Degussa AG, Frankfurt, Germany), a known mixture of 80% anatase and 20% rutile with an average particle size of 30 nm and a reactive surface area of 50 ± 15 m² g⁻¹, was used for the photocatalytic experiments. IC Acrodisc® 13 mm syringe filter with 0.2 µm Supor® (PES) membrane (Pall Corporation, Milan, Italy) were used before HPLC injection.

2.2. Analytical determination

The HPLC system consists of a pump Series 200 (Perkin Elmer) equipped with vacuum degasser and a programmable FD. The fluorescence excitation/emission wavelengths selected were 280/500 for LEV, 297/507 nm for MAR, 290–500 for MOX and 280/450 nm for the other analytes. After an equilibration period of 10 min, 50 µL of each sample were injected into a 250 × 4.6 mm, 5 µm Ascentis RP-Amide (Supelco) coupled with a similar guard-column. The mobile phase was 25 mM H₃PO₄–ACN (85:15), except for MOX (80:20), for 30 min, followed by a 1 min-linear gradient to 100% ACN. After washing for 5 min, the initial conditions were re-established by a 1 min-linear gradient, at a flow rate of 1 mL min⁻¹.

The HPLC–ESI-MS/MS was performed by using an Agilent 1100 HPLC with a Luna C18 (150 × 4.6 mm, 5 µm) column, maintained at 30 °C. The mobile phase was HCOOH 0.5%, v/v in ultrapure water–ACN (85:15) for MOX and (90:10) for the other analytes. The flow rate was 1.2 mL min⁻¹ and the injection volume was 5 µL. The MS/MS-system consisted of a linear trap Thermo LXQ. ESI experiments were carried out in positive-ion mode under the following constant instrumental conditions: source voltage of 4.5 kV, capillary voltage of 20 V, capillary temperature of 275 °C and normalized-collision energy 35.

The HPLC–UV system consists of a PU-1580 pump (JASCO) equipped with a programmable UV-1575 UV–vis detector (JASCO). The analysis wavelength selected for all FQs was 275 nm. 20 µL of each sample were injected into a 150 × 4.6 mm, 5 µm Symmetry Column (Waters) coupled with a similar guard-column. The mobile phase was water (pH adjusted to 2.5 with 37% HCl)–ACN (90:10) except for MOX (85:15) for 30 min, at a flow rate of 1.2 mL min⁻¹.

2.3. Kinetic experiments

Irradiation was carried out in Pavia (45° 11' N, 9° 09' E, July 2011, 10.00 a.m.–4.00 p.m., 27–30 °C) under natural sunlight. The incident power was measured by means of a HD 9221 (Delta OHM) (450–950 nm) and a Multimeter (CO.FO.ME.GRA) (295–400 nm) pyranometers and resulted to be in the range 290–470 W m⁻² (Vis) and 20–31 W m⁻² (UV). Batch experiments were typically performed in a 500 mL open glass container (20 mm depth, exposed surface 280 × 200 mm) under magnetic stirring on the window ledge.

2.4. Sample preparation

With the target of assessing the efficiency of the photo(cata)lytic process for FQs remediation in a actual matrix, all the experiments were carried out on raw surface water samples (pH 7.7 ± 0.1, conductivity 232 µS cm⁻¹, DOC 0.97 mg L⁻¹, calcium 25 mg L⁻¹, magnesium 5 mg L⁻¹, iron 82 µg L⁻¹, manganese 10 µg L⁻¹, chloride 9 mg L⁻¹, nitrate 6.5 mg L⁻¹, sulfate 29.3 mg L⁻¹) collected in the Ticino river (0–30 cm depth) in Pavia. In order *not* to remove suspended particles and DOM, which may affect the photodecomposition kinetics (see Section 3), filtration was omitted. The amount of native FQs was negligible, being below the instrumental detection limits (IDLs). Before irradiation, samples were individually fortified with 20 µg L⁻¹ of DAN, which is indeed the most FD-sensitive FQ [44], and 50 µg L⁻¹ of the other FQs.

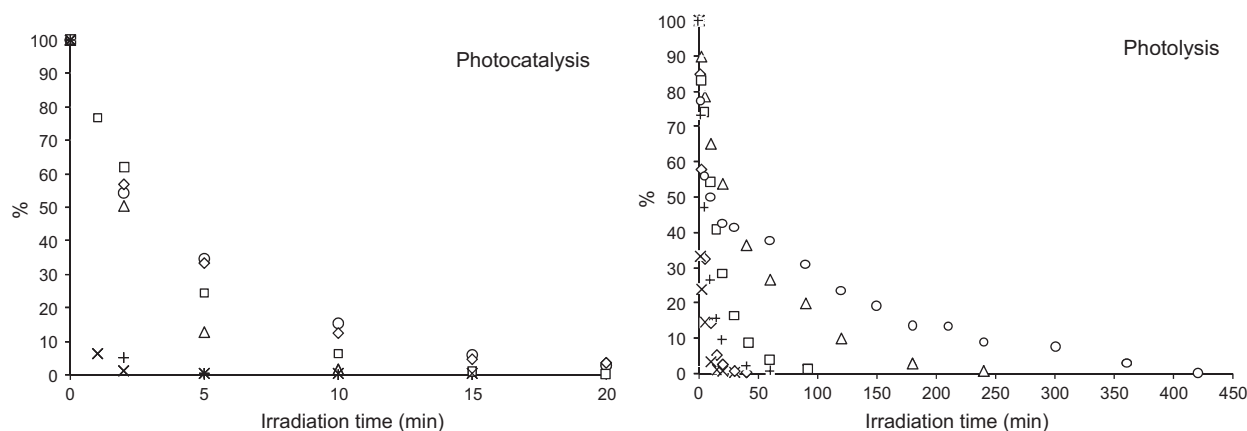


Fig. 1. Degradation profiles obtained under natural sunlight TiO_2 photocatalysis and direct photolysis in raw river water for CIP (\diamond), DAN (\times), ENR ($+$), LEV (Δ), MAR (\square) and MOX (\circ). IDLs: $0.1\text{--}0.3\ \mu\text{g L}^{-1}$; RSD $< 5\%$, $n = 3$.

Titania suspensions ($0.5\ \text{g L}^{-1}$) were magnetically stirred in the dark for variable frame times (20–60 min), depending on the specific analyte, to promote FQs adsorption on the catalyst surface. During the irradiation course, aliquots (1 mL) of each sample (500 mL) were withdrawn at the specific times, and promptly injected in the HPLC-FD system. In the case of titania, suspension aliquots were filtered ($0.2\ \mu\text{m}$).

In order to build up a sufficiently large concentration of photo-products to make LC/MS analysis easy, a set of experiments for the identification of FQs photoproducts was carried out under different conditions. 10 mL portions of $10^{-3}\ \text{M}$ (357, 331, 359, 361, 401, 362 mg L^{-1} respectively for DAN, CIP, ENR, LEV, MOX, MAR) aqueous solutions (deionized water) of each FQ containing $0.5\ \text{g L}^{-1}$ of the photocatalyst were magnetically stirred in the dark overnight in order to ensure FQs adsorption on the catalyst surface and then irradiated in a 25 mL open quartz vessel with continuous magnetic stirring by means of two 20 W phosphorus-covered low pressure mercury arcs with emission maximum centered at 310 nm (UV flux measured by a 310 nm sensitive probe, $12\ \text{W m}^{-2}$). The result upon direct photolysis was compared by irradiating identical 10 mL samples of the same solutions omitting the photocatalyst in a quartz tube by using a multilamp apparatus fitted with ten 15 W phosphorus-coated low pressure mercury arc with maximum emission centered at 310 nm. The irradiated samples were immediately analyzed by HPLC-UV prior HPLC-ESI-MS/MS analysis.

3. Results and discussion

3.1. Reaction kinetics

The remediation of trace level contaminants present in natural waters is a demanding task, because actual environmental matrices contain different species present at variable amounts that are sensitive to the TiO_2 photo-oxidation [17], such as DOM. This is especially true for non-selective AOPs, as UV- TiO_2 photocatalysis is [17].

Photo(cata)lysis was carried out in untreated river water with natural sunlight as the light source, and at FQ concentration in the range of few tens of ppb, based on the amounts reported in literature [4].

Contrary to previous reports [10,17,21] samples were not purged with either oxygen or CO_2 -free air, in order to take into account the role of dissolved oxygen naturally present in the air-equilibrated solution.

As it will be shown below, all of the drugs proved to be susceptible to photodegradation under sunlight outdoor conditions. Indeed they were degraded down to below the IDLs ($0.1\text{--}0.3\ \mu\text{g L}^{-1}$) with good reproducibility (RSD $< 5\%$, $n = 3$). Fig. 1 shows the decomposition profiles of each substrate as observed in river water under direct and TiO_2 -promoted photolysis. All experimental data were fitted by a first order exponential law, as determined by a dedicated software (Fig. P application, Fig. P Software Corporation). The kinetic constants obtained in this way are more accurate than the commonly adopted linear correlation in the $\ln [C]/[C_0]$ versus irradiation time plot, which gives an undue weight to the first points of the degradation profile.

As apparent in Table 1, reporting the kinetic constants and the pre-exponential factors of the decays, the photocatalysis data were fitted in all of the cases by a mono-exponential law (rate constant k), while upon direct photolysis a mono exponential fitting was satisfactory only for CIP and MAR, a bi-exponential one (rate constants k , h) resulted more accurate for the other four drugs. The bi-exponential decay was already observed for FQs [16] and refers to the role of two ionic forms. Except for the case of CIP, the drug degradation was faster in presence of the photocatalyst. Under such conditions, the degradation rate constants (k) were found to be from two to five times faster than in direct photolysis, with more than 90% removal in 15 min.

The pH has been previously shown to affect the degradation, both upon photolysis [16] and TiO_2 -photocatalysis [19–21]. In the present study, FQ removal is very efficient at “natural” pH, that is in non tampered river water, as in previous work [20]. As a matter of fact, the pH is of primary importance, as it is the key parameter in controlling the adsorption equilibrium of the substrate on the catalyst surface and indeed the photocatalytic FQ degradation rate is proportional to the fraction of FQ adsorbed [21]. On the basis of the FQs dissociation constants (pK_a) [4], it can be concluded that in the aqueous matrix studied here [$\text{pH } 7.7 \pm 0.1$] FQs are present mainly in the zwitterionic form, the most easily sorbed species under these conditions [21]. In our experiments, the maximum adsorption, in good agreement with recent literature [10,17], was reached in 20 min for ENR (9%) and MAR (7%), 40 min for DAN (9%) and MOX (5%), 1 h for CIP (12%) and LEV (6%). In any case, equilibration by stirring for 2 h caused no further adsorption.

These results are particularly informative for evaluating the validity of AOP remediation of FQs in actual matrices, because these include any effect related to the presence of DOM, and probably of other anthropogenic pharmaceuticals/chemicals, as well as metal

Table 1TiO₂ photocatalysis and direct photolysis degradation kinetic constants (*k*, *h*) determined for each FQ in raw river water under natural sunlight.

| FQ | Photolysis | | | | | Photocatalysis | | |
|-----|-------------------------------|-----------------------|-------------------------------|-----------------------|--------------|-------------------------------|-----------------------|--------------|
| | <i>k</i> (min ⁻¹) | <i>A</i> [*] | <i>h</i> (min ⁻¹) | <i>B</i> [*] | Main process | <i>k</i> (min ⁻¹) | <i>A</i> [*] | Main process |
| CIP | 0.22 (2) | 100 (3) | – | – | (i) | 0.22 (2) | 100 (3) | (iii) |
| DAN | 0.66 (3) | 89 (3) | 0.12 (2) | 10 (3) | (i–iii) | 2.78 (6) | 100 (3) | (iii) |
| ENR | 0.24 (3) | 51 (9) | 0.08 (1) | 49 (9) | (i–iii) | 0.42 (2) | 99 (2) | (iii) |
| LEV | 0.19 (2) | 26 (2) | 0.0174 (5) | 74 (2) | (i–iii) | 0.36 (1) | 100 (1) | (iii) |
| MAR | 0.061 (2) | 100 (1) | – | – | (iv) | 0.27 (1) | 101 (1) | (iii) |
| MOX | 0.34 (4) | 50 (2) | 0.0065 (4) | 51 (2) | (i–iii) | 1.50 (2) | 100 (1) | (iii) |

^{*} *A* and *B* are the pre-exponential factors.

oxides naturally occurring in environmental waters, in particular redox-active metal species, such as iron and manganese oxides.

3.2. FQs photodegradation paths

In the following, the reaction paths upon direct irradiation in aqueous solution (subscript _W) and upon photocatalysis (subscript _T) are briefly illustrated. The structures of the photoproducts were suggested on the basis of the HPLC–ESI–MS/MS chromatograms, MS/MS fragmentations of each FQ (as reported in [Supplementary data section](#)), the HPLC retention times, and also diagnostic of the chemical functions present and the comparison with literature data [16,43–51].

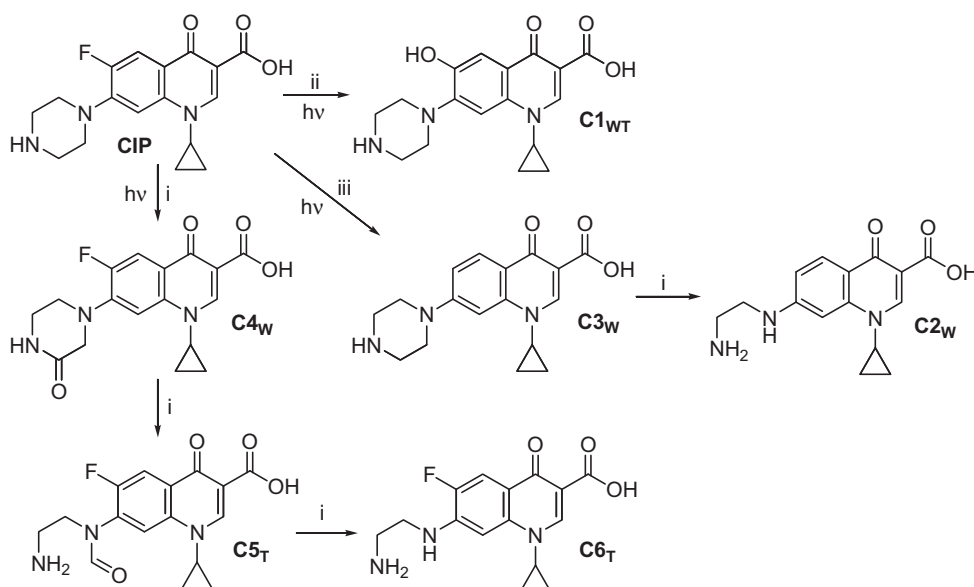
The main product from direct irradiation of CIP resulted from substitution of the fluorine in position 6 by a hydroxyl group (C1_{WT}, see [Fig. 2](#)), compare [45]. Of the three minor products, two (C3_W, C2_W) arose from reductive dehalogenation and, in the latter case, subsequent oxidative degradation of the piperazine ring (compare [45]), the last one (C4_W) to conversion of the amine function to amide (the analogue from ENR has been characterized [16,46]). TiO₂ photocatalysis, on the other hand, yielded a small amount of C1_{WT}, reasonably from competitive direct light absorption by CIP, and two products (C5_T, C6_T, the latter one largely predominant, had been previously identified [46]). These were rationalized as arising from C4_W by further amine side-chain oxidation.

Direct irradiation of DAN gave two main products (D3_{WT}, D4_W, see [Fig. 3](#)), the former one, arising by OH/F substitution, previously identified by Liu et al. [52], the latter one from reductive dehalogenation. Four minor products (D1_W, D2_W, D5_W, D6_{WT}) were obtained, the last one arising by oxidative demethylation of the

aliphatic amine moiety, compare [52,53], and the other ones by subsequent oxidation of the above primary photoproducts (D1_W has been previously reported by Ge et al. [53]). As for photocatalysis, this gave two products, viz. D3_{WT} (from direct absorption) and D6_{WT} (from oxidative demethylation of the amine side-chain), with the latter largely predominant.

Direct irradiation of ENR gave nine products in appreciable amounts (E_{WT}, B_{WT}, D_{WT}, A_W, C_W, E1_W, E2_W, E3_W, E4_W), some of which had been previously characterized [16,45–50] (see [Fig. 4](#)). The structures were assigned on the basis of mass spectra and retention times, as well as by analogy with previous more extensive characterizations for the reaction in solution. Products E_{WT}, B_{WT}, D_{WT}, A_W, C_W had already been characterized in our previous works and their structure was attributed by comparison of the mass spectra with our previous data. These result from piperazine ring oxidation (E_{WT}), F/OH substitution (D_{WT}) and reductive defluorination (A_W), in all of the cases followed by further degradation via side-chain oxidation of the piperazine moiety (B_{WT}, C_W as well as the previously not reported E1–4_W). On the other hand, photocatalysis gave six products in appreciable amounts, viz. the above E_{WT}, B_{WT} and D_{WT}, as well as products from the further oxidation of E_{WT} (Q_T, O_T, E5_T, previously characterized [16,46,47]), as shown in [Fig. 4](#). All of these resulted from sequential oxidation of the amine side-chain.

Seven products were formed in photolytic degradation of LEV (L1_W, L2_W, L3_W, L4_W, L5_{WT}, L6_{WT}, L7_{WT}, see [Fig. 5](#)). The most abundant ones were L7_{WT} [53] and L6_{WT} [12]. The minor ones resulted from LEV via solvolysis of the fluorine (L5_{WT}) and reductive defluorination (L4_{WT}), followed in both cases by oxidative degradation of the amine side-chain (L2_W and respectively L1_W, L3_W and L4_W).

**Fig. 2.** Degradation paths and byproducts in the photolysis (W) and photocatalysis (T) of CIP.

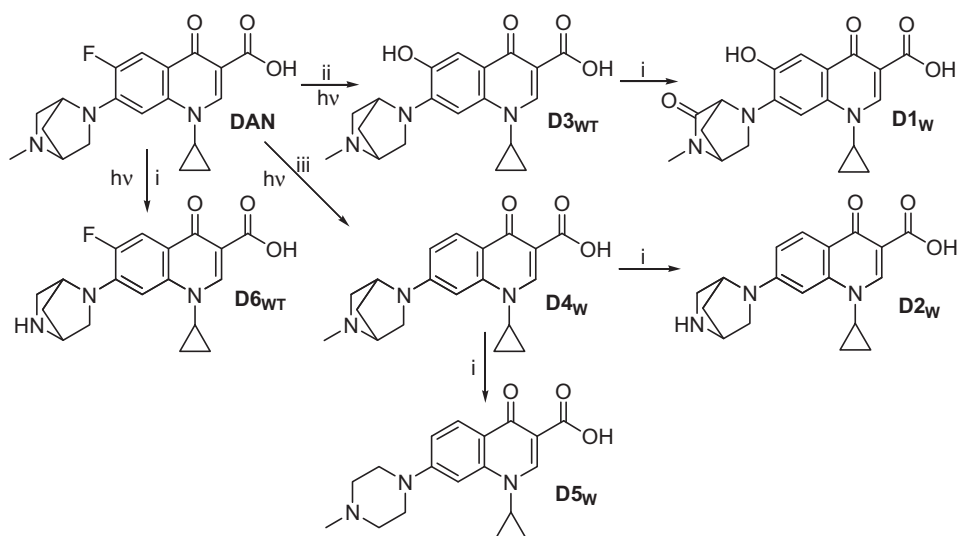


Fig. 3. Degradation paths and byproducts in the photolysis (W) and photocatalysis (T) of DAN.

Apart from a small amount of L5_{WT} from direct photolysis, the products obtained upon photocatalysis all resulted from amine side-chain oxidative degradation, leading to L7_{WT} and L9_T from it as well as to L8_T via a different oxidation path.

As for MAR, direct irradiation led to a peculiar process, cleavage of the dihydrooxadiazine ring to give two main products (F_{WT} and G_W, see Fig. 6) (compare [16,51]). Photocatalysis, on the other hand, gave some F_{WT} by competitive direct excitation along with two products, Ma1_T, Ma2_T, arising from stepwise oxidative degradation of MAR involving the piperazine side-chain.

To the best of our knowledge the photochemistry of MOX has not been previously reported. Photolysis in aqueous solution gave six products resulting from OH/F substitution (M3_{WT} and M1_{WT}, M2_{WT} by further oxidation), reductive dehalogenation combined with side-chain oxidation (M6_W and M5_W) and side-chain oxidation (M4_{WT}) in roughly equivalent amounts. On the other hand, photocatalysis gave tiny amounts of M3_{WT} and its degradation products (M10_T, M2_{WT}, and M1_{WT}) while the main products resulted from primary oxidative degradation of the amine side-chain M4_{WT} (along with M9_T, M8_T, M7_T and M11_T) (see Fig. 7).

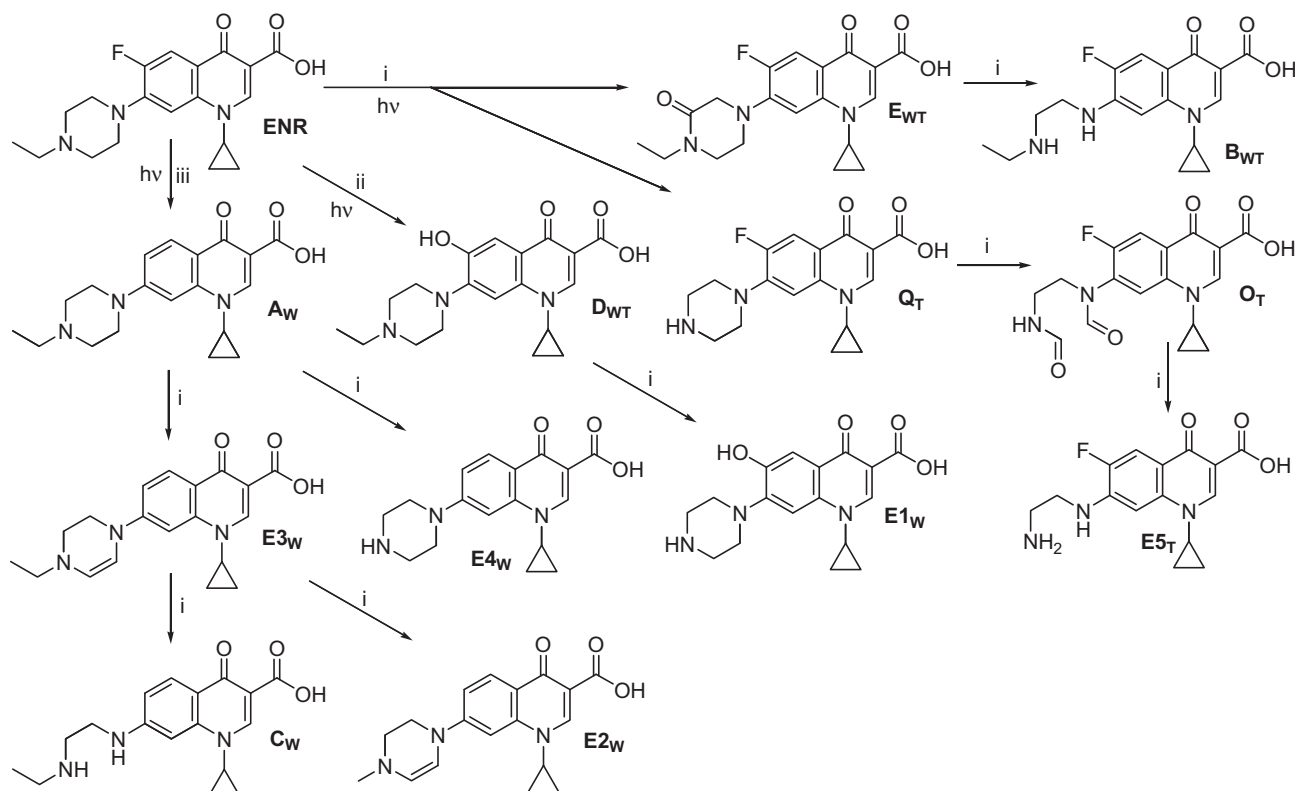


Fig. 4. Degradation paths and byproducts in the photolysis (W) and photocatalysis (T) of ENR. Compounds labeling is the same as reported in Ref. [16].

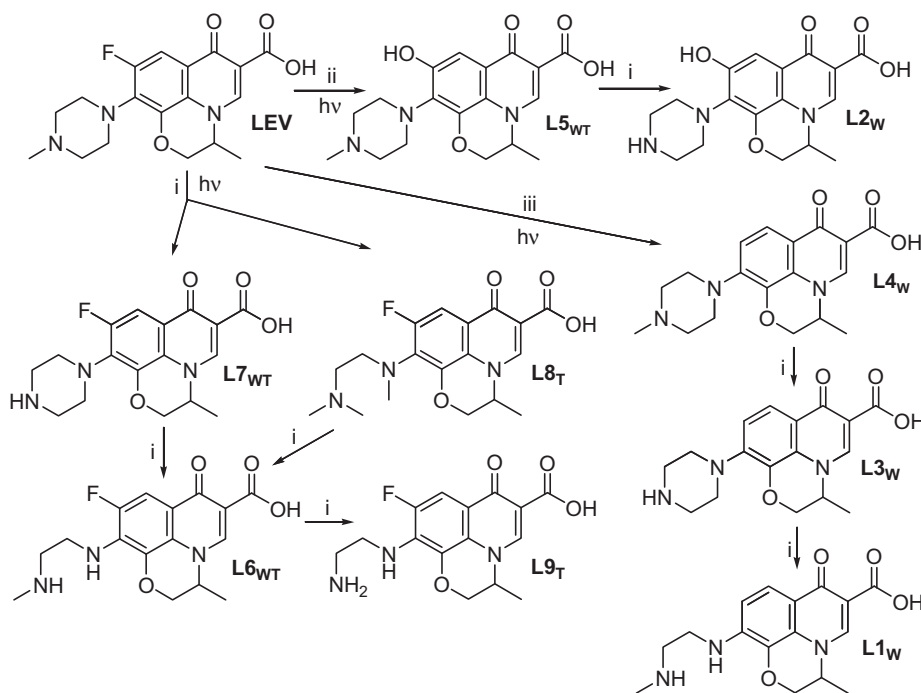


Fig. 5. Degradation paths and byproducts in the photolysis (W) and photocatalysis (T) of LEV.

3.3. Mechanistic issues

The photochemistry of several FQs by direct irradiation in water has been previously examined in depth. The present study in 'natural' water shows no change in the pattern observed, with the previously not investigated MOX behaving analogously, and demonstrates again two types of reactions. The first one includes unimolecular photoreactions; these proceed via the triplet state [54] and involve either (i) photosubstitution of fluorine on carbon 6 of the aromatic moiety by an hydroxyl group or (ii) reductive dehalogenation [54]. The efficiency of these processes varies with the structure, and is lowered by electron-donating groups (see the effect of a OMe group in LEV).

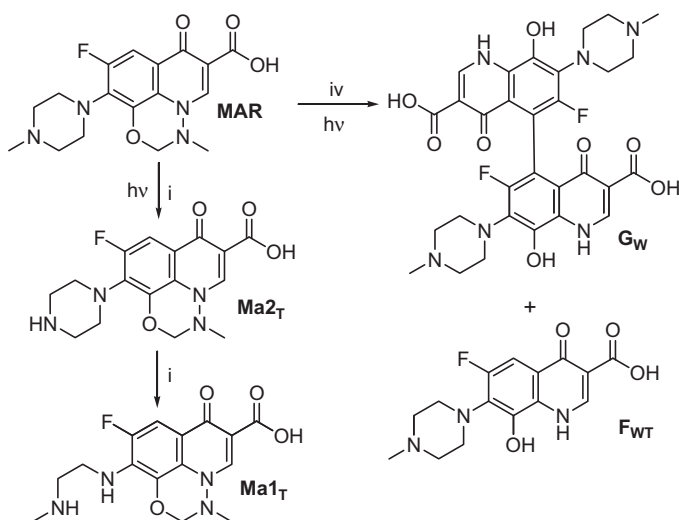


Fig. 6. Degradation paths and byproducts in the photolysis (W) and photocatalysis (T) of MAR. Compounds labeling is the same as reported in Ref. [16].

The second type includes (iii) bimolecular reactions where the excited state of the drug or of some impurity attacks the drug causing electron or hydrogen transfer from the electron-rich moiety present, viz. the amino side-chain (see Fig. 8). This is a general process (except for MAR, which as mentioned, has a competing outcome, N–N bond cleavage, indicated in the Table as path (iv)) the efficiency of which appears to depend on the structure of the amine side-chain. In fact, this process is more important with tertiary than with secondary amines and with five rather than six-membered rings. Thus, the fastest decomposing FQs are DAN and MOX, bearing a 2,5-diazabicyclo[2.2.1]hexane and a 2,8-diazabicyclo[4.1.0]nonane side-chain, respectively. The excitation of DOM may have an important role when the monomolecular processes from the excited state are slow, e.g. the rather efficient degradation of DAN may be due to overwhelming side-chain degradation initiated by H abstraction. In the photocatalytic process, a sizeable fraction of impinging light is absorbed by FQs (ϵ ca. $10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) and this yields the same products as above in a minor amount via path (i) or path (ii). Most of the light is absorbed by the titania particles, at the present TiO_2 concentration [17,21], which then interact by hydrogen or electron transfer with the adsorbed drug. Thus, the chemical path is now only path (iii), and the predominance of DAN and MOX becomes more marked.

As for the kinetics of the reaction, at the low concentrations used here (and present in the environment) degradation obeys to a first order law upon direct irradiation, because light absorption is proportional to the concentration [16]. The fitting by a biexponential law in several cases may be due to the formation of a second ionic component, even if to a lesser extent. A first order kinetics is obeyed also in photocatalysis, but in that case adsorption equilibria are involved.

3.4. Secondary photoprocesses

A key point for judging the significance of the method for water recovery, is not so much that the drug is degraded, but

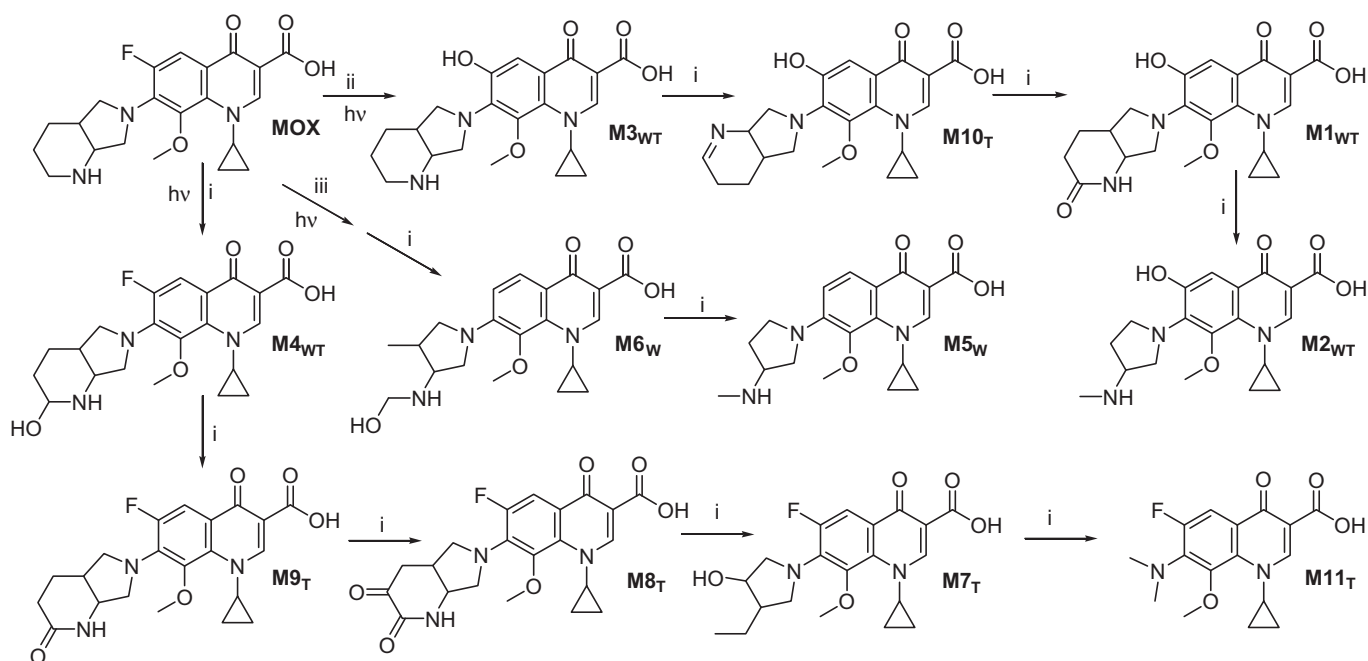


Fig. 7. Degradation paths and byproducts in the photolysis (W) and photocatalysis (T) of MOX.

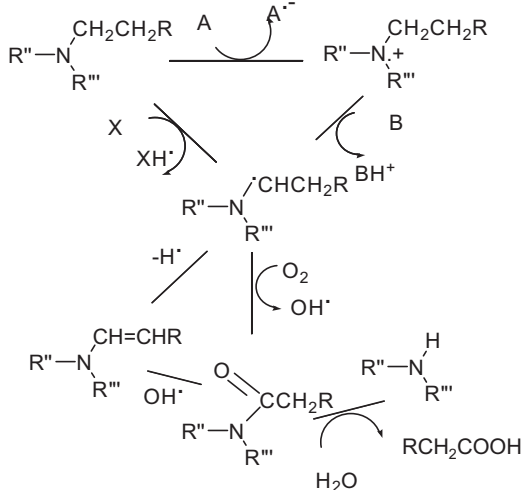


Fig. 8. Bimolecular photoreaction paths for selected FQs.

that the antimicrobial activity is abated [17]. In the case of FQs, the activity is linked more to the quinolone core than to the substituent pattern [10]. In the primary degradation presented here, the photo(cata)lytic primary byproducts conserved the quinolone core but were themselves degraded both by direct irradiation and by photocatalysis. On a longer time scale such secondary photoreactions are known to cause the degradation of the heterocycle ring [16,46,48,49]. The action of a strong photo-oxidant such as TiO_2 appeared to accelerate the last reactions resulting in lifetimes of the intermediates of the same order of that of the starting material. As an example, Fig. 9 shows the evolution and decay curves of MOX degradation intermediates, obtained by HPLC-FD analysis. As can be noticed, the lifetime of the products observed is markedly shortened in the photocatalytic process.

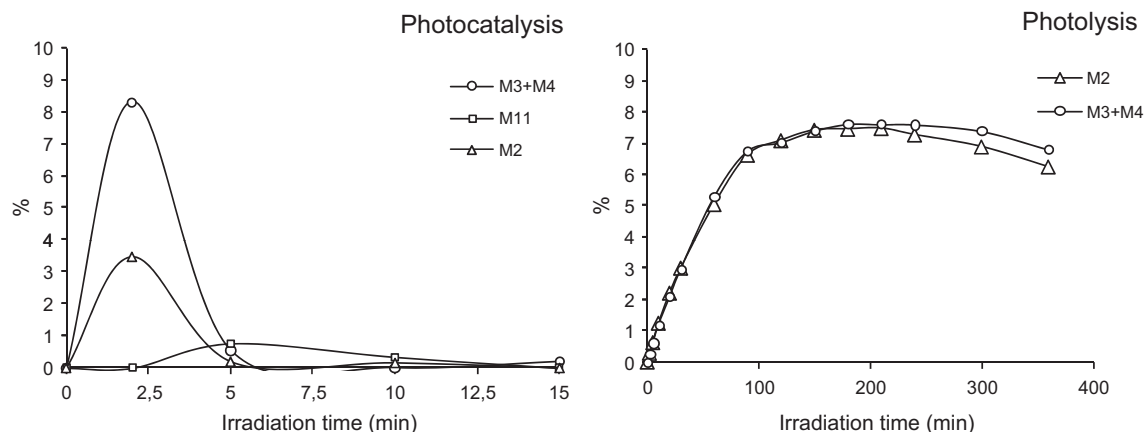


Fig. 9. Temporal evolution profiles of MOX byproducts observed in raw river water under natural sunlight TiO_2 photocatalysis and direct photolysis.

4. Conclusions

The present investigation proves the effectiveness of the TiO_2 photocatalytic treatment for the remediation of various FQs present in surface water at the ppb levels. Degradation rates were found to be from two to five times larger in comparison with direct photolysis, resulting in a substantial removal of the starting antibiotic in about 15 min under natural sunlight. The products arose exclusively from the oxidative degradation of the amine side-chain, to the exclusion of the processes involving the fluorine atom that participate, or are even predominant upon direct irradiation, as is the case of CIP. Comparing the product distribution under the two conditions allows to distinguish the structure requirements for fast amine moiety degradation (tertiary > secondary amines, five > six-membered), a result that should have predictive value. The primary products, identified by HPLC–ESI-MS/MS, were themselves degraded. Their lifetime, comparable to that of the parent compounds, was strongly shortened in presence of the catalyst and under these conditions the FQ oxo-quinoline carboxylate core, responsible for the retention of the antimicrobial activity, was finally degraded. Therefore, the TiO_2 photocatalyzed oxidation proved to be a valid remediation procedure for the target compounds also in the presence of matrix interferences, such as DOM or other anthropogenic organic molecules usually present in surface water. Good decomposition rates were observed under natural sunlight, thus supporting the use of solar light as a green power source. Therefore, the method is certainly suitable for the end-of-pipe remediation of pre-treated water from such persistent pollutants.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2012.02.008.

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